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RESULTS OF THE LOW FLOW CARBON FILTER WHEN USED AS A PESTICIDE SAMPLER

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ABSTRACT

The Klamath Basin Study, a special project of the Federal Water Pollution Control Administration, is studying pesticides in irrigation water. One of the tools utilized for sampling the water is the low-flow carbon filter. Pesticide determination in discrete water samples and week long carbon filter composites are compared. In the two types of sampling, endrin showed good comparison; DDT series pesticides did not.

KBS Technical Paper No. 1
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21
19

TABLE OF CONTENTS

	Page
INTRODUCTION	1
SAMPLING STATIONS & COLLECTION PROCEDURE	1
LABORATORY PROCEDURES	3
ANALYTICAL LIMITS OF LABORATORY PROCEDURES	
WATER	3
CARBON COLUMNS	4
DISCUSSION OF RESULTS	5
SUMMARY & CONCLUSIONS	8

I

LIST OF FIGURES & TABLES

FIGURES

		Page
I	Schematic, Model LF-1 Organics Sampler	10
II	Lost River System	11
III	Graphical Comparison of Water vs. Carbon	12

TABLES

I	Graphical Comparison of Water vs. Carbon Indian Springs	13
II	Carbon Filters vs. Water Samples Pump "D"	16
III	Results of Carbon Column with Glass Wool	18

RESULTS OF THE LOW FLOW CARBON FILTER WHEN USED AS A PESTICIDE SAMPLER

Introduction

During 1960-61 extensive water fowl kills occurred in the Tule Lake-Lower Klamath National Wildlife Refuges. In 1963, the U.S. Fish and Wildlife Service established that the deaths were caused by pesticides. At that time, the States of Oregon and California and the U.S. Fish and Wildlife Service requested U.S. Public Health Service's technical assistance in determining the source and movement of pesticides in and around the refuges. The Klamath Basin Study was initiated in December 1963 to study this water pollution problem.

The engineering staff of the Klamath Basin Study initiated a water sampling program of collecting discrete water "grab" samples at regular intervals throughout the Lost River system. As an adjunct to this program, the low flow carbon filter was used to continuously sample the stream. The "grab" samples were to give instantaneous pesticide concentration values and the carbon filter was to provide a measure of average concentrations over a period of time. In order to sample the same water as the carbon filter, "grab" samples were taken at the exit of the bypass valve (Point C on Figure 1).

This paper reports the results of the use of the low flow carbon filter as a sampler of pesticides in water.

Sampling Stations and Collection Procedure

In conventional operation of the low flow carbon filter, approximately 1200 liters of water are pumped through an all-fines carbon

column three inches in diameter and eighteen inches long (Figure 1). Organics, including pesticides, in the water are adsorbed from the water onto the carbon. In the laboratory, pesticides are desorbed from the carbon using chloroform as a solvent.

The "grab" sample program soon indicated that the pesticides used were appearing in relatively larger amounts in the Tulelake end of the Lost River Basin. Therefore, the two carbon filter panels were installed at approximately the entrance and exit for the irrigation water of Tulelake Irrigation District (TID). Figure 2, a schematic of the Lost River Basin, shows the location of the two panels. Indian Springs (location of first panel) is located on the Lost River about six miles upstream of the Lower Lost River Diversion Dam. This dam diverts water to the "J" Canal which supplies essentially all of the irrigation water to TID. Return flow within TID is collected in a series of drain canals all of which empty into Tule Lake Sump. Pump "D" (the location of the second panel) regulates the level of the Tule Lake Sump by exporting the water via a tunnel through the hill to Lower Klamath Lake.

At pump "D", water is sampled at the exit side of a 60 cfs irrigation drainage pump. At Indian Springs (the entrance panel), water is supplied to the panel by an Oberdorfer bronze rotary gear pump driven by a 1/3 hp electric motor. The tubing inlet is placed in the moving part of the two feet deep stream approximately fifteen feet from shore. The end of the tubing is protected by a strainer with 1/8 x 1 inch slots. The end of the tubing is bent upward slightly so that the intake is several inches above the stream bed.

The two gallon "grab" sample is collected in two 1-gallon glass jugs with an aluminum foil liner insulating the cap. Prior to use bottles are washed with detergent and thoroughly rinsed to remove all traces of detergent. In the field the jugs are again rinsed in the stream prior to the collection of the sample.

Laboratory Procedures

In the laboratory, pesticides are extracted from a 3-liter aliquot of the "grab" sample in a three step process using a mixture of 10% ethyl ether in petroleum ether. The extract is eluted through a Florisil column for cleanup.

The carbon columns are first air dried at room temperature and then extracted with chloroform in a large soxhlet for forty hours. Partitioning and cleanup are accomplished using acetonitrile, ethyl and petroleum ether mixtures and Florisil.

These procedures are described in detail by the Project Chemist, R. E. White, in his paper, "Insecticide Analysis Procedures Used by the Klamath Basin Study".[1]

Analytical Limits of Laboratory Procedures

Water

The procedures established by the Study's laboratory are able to detect the chlorinated hydrocarbon compounds, DDE, DDD, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, thiodan, and BHC at an approximate sensitivity of 0.005 parts per billion (ppb) in a

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[1] Presented at the Pacific Northwest Pollution Control Association, Vancouver, British Columbia, November 3-5, 1965

3-kilogram water sample. The sensitivity for DDT and chlordane is 0.010 ppb and for toxaphene 0.050 ppb. In addition to these specific compounds, the water samples are also analyzed to determine total chlorinated hydrocarbon, based on a 50% halogen content. This measurement is possible due to unique specificity of the Dohrmann microcoulometric system to chlorinated hydrocarbons.

In the analysis of water, one often finds chlorinated hydrocarbons which cannot be specifically categorized. Since all of the chlorinated hydrocarbon group are man-made pesticides, it is logical to assume that the unidentifiable materials are metabolites of pesticides used in the project area. While these "unknowns" cannot be related to specific toxicities to biota of the system, they are an indication of the amounts of pesticide being washed into the water community. These "unknowns" are included in the total chlorinated hydrocarbon content of the samples here reported.

CARBON COLUMNS

Due to the 400 times larger sample size, the analytical procedures are significantly more sensitive to pesticides recovered by the carbon columns. The sensitivity for DDE, DDD, DDT, heptachlor, heptachlor epoxide, chlordane, dieldrin, and endrin is approximately 0.00015 ppb. Due to the unknown and variable background of the carbon, it is not possible to calculate a maximum total chlorinated hydrocarbon content of the carbon column extracts.

Discussion of Results

Tables I and II show the results of carbon and water analyses for the two locations - Indian Springs and Pump "D". The table shows only those identifiable compounds which were actually found in addition to total chlorinated hydrocarbons.

Comparing the water and carbon analyses shown in Table I, the carbon filter method appears to be much more responsive to some pesticides than others. For instance, there appears to be no correlation between the sampling methods under DDE, DDD and DDT, heptachlor, and heptachlor epoxide. There is not enough information about dieldrin to make a positive evaluation, since the levels found in the carbon are just below the approximate 0.005 ppb limit of detection in the water samples. To increase the sensitivity in the water sample to that of the carbon sample, the size of the water sample would have to be increased at least five times; this is neither practicable nor was the concentration of dieldrin in the water significant enough to warrant this.

Endrin results show a good comparison at the Indian Springs station. Figure 3 is a graph of endrin concentration for the water samples and carbon filter extracts. No explanation can be offered as to why the second carbon filter run was not closer to the "grab" sample analysis. However, the next four runs do approximate the water results. After October the endrin level in the water fell below the sensitivity of the procedures utilized by the Klamath Basin Study. The significant point is that the carbon filter results

did represent a good average value of the endrin concentrations for the water "grab" samples shown.

At Pump "D", as shown in Table II, endrin and dieldrin were consistently found, but only on the carbon extracts and there at a level below the detection limit for water samples; therefore no comparisons can be made. The DDE, DDD, and DDT results at Pump "D" are similar to those at Indian Springs. In general, the Pump "D" carbon extract results were much lower than the discrete water samples. However, due to a malfunction, the last two carbon filter samples collected at Pump "D" represent about five times smaller than "normal" volumes of water. It appears from these two samples that the pesticide determinations for the DDT series in the lower-volume carbon filter sample compare more favorably with those in the "grab" samples than do the larger-volume carbon filters.

Blank spaces in Table II can be taken to indicate (1) that the compound was not present in detectable concentration or (2) if present, was either not adsorbed on or was not desorbed from the carbon.

To check on the desorption process, solvents other than chloroform followed its use, including benzine, acetone and mixtures of the two, with no significant change in the results obtained.

The adsorption process was also explored for the possibility that some of the pesticide in the discrete water is on particles in the water which are partly retained on the carbon and partly washed through the carbon filter without losing this pesticide residue load to the carbon. Approximately one-half inch of tightly

packed glass wool was placed on the inlet end of each of two carbon filters. One carbon filter so packed was used at each station. Realizing that the size range of particles stopped by the glass wool cannot be accurately defined, it was believed that larger particles, such as algae, chlodocera, and detritus would be stopped. This was confirmed visually by the fact that previously the algae would give a greenish tint to the carbon as much as one third of the way up the carbon. This condition was not observed with the glass wool in place.

The results, shown in Table III, are as follows: The filter at Indian Springs sampled 1257 liters of water. On the glass wool, DDE, DDD and/or DDT, and a chlordane-like substance were each found at a level of 2 ppb, based on the damp weight of sediment and glass wool. Converting this to a more meaningful value, if all of these pesticides caught on the glass wool had instead been extracted with the carbon, then the apparent concentration in the 1257 liters of water would have increased by .000085 ppb (.085 pptr) for each of these pesticides. As a percentage of the total amount of pesticide in the wool and carbon extracts, this amount on the wool amounts to 19% for DDE, 0% for DDD and DDT, and 50% for the chlordane-like substance.

At the Indian Springs station dieldrin and endrin results indicate that less than 1 and 9% respectively of the total amount was in the glass wool extract. At Pump "D", dieldrin and endrin were found in the carbon extract but not in the glass wool.

However, for reasons not gone into here, the analytical sensitivity for this glass wool sample was not as good as it was for any previous sample at that station. If the Pump "D" glass wool sample is assumed to have an amount of pesticide equal to the sensitivity, then this could be considered to be the upper limit of the amount in the sample. Doing this would indicate a maximum of 66% dieldrin and 50% endrin on the Pump "D" glass wool. These percentages are rather high; if the same amounts were present at Pump "D" as at the Indian Springs stations, the percentages would be approximately 1 and 5% respectively.

Summary and Conclusions

1. The low flow carbon filter does extract and concentrate pesticide from water.

2. Based on limited data, the method gives a reliable average concentration of endrin in the water sampled when compared with results from "grab" sample analyses.

3. Data for the DDT series of pesticides derived from 1200-liter carbon filter water samples do not compare favorably with data derived from "grab" samples. Limited data indicate, however, that DDT comparison under the two methods of sampling improved when a 200-liter water sample is used in the carbon filter process.

4. Sediment in the water, as represented by the amount caught on a glass wool filter, has a minimal effect on pesticide sampling efficiency.

5. These are to be considered as preliminary conclusions only, and the engineering staff of the Klamath Basin Study will continue its carbon filter investigations during the 1966 irrigation season.

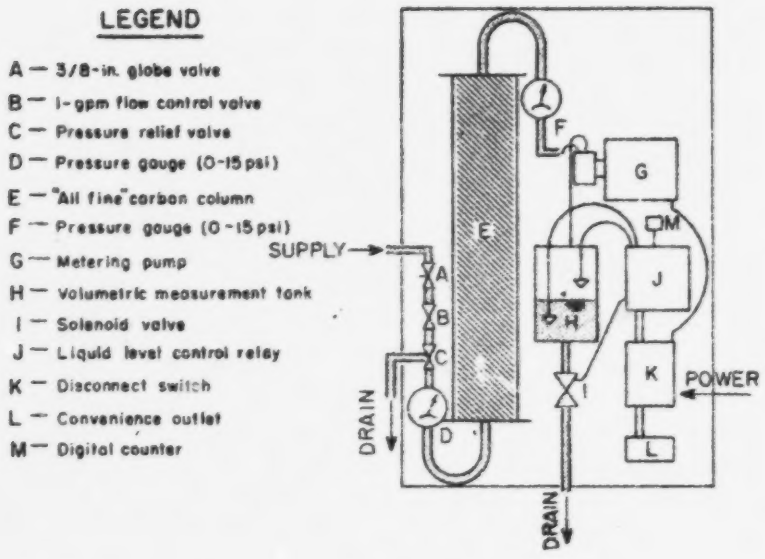

Figure 1. Schematic, Model LF-1 organics sampler.

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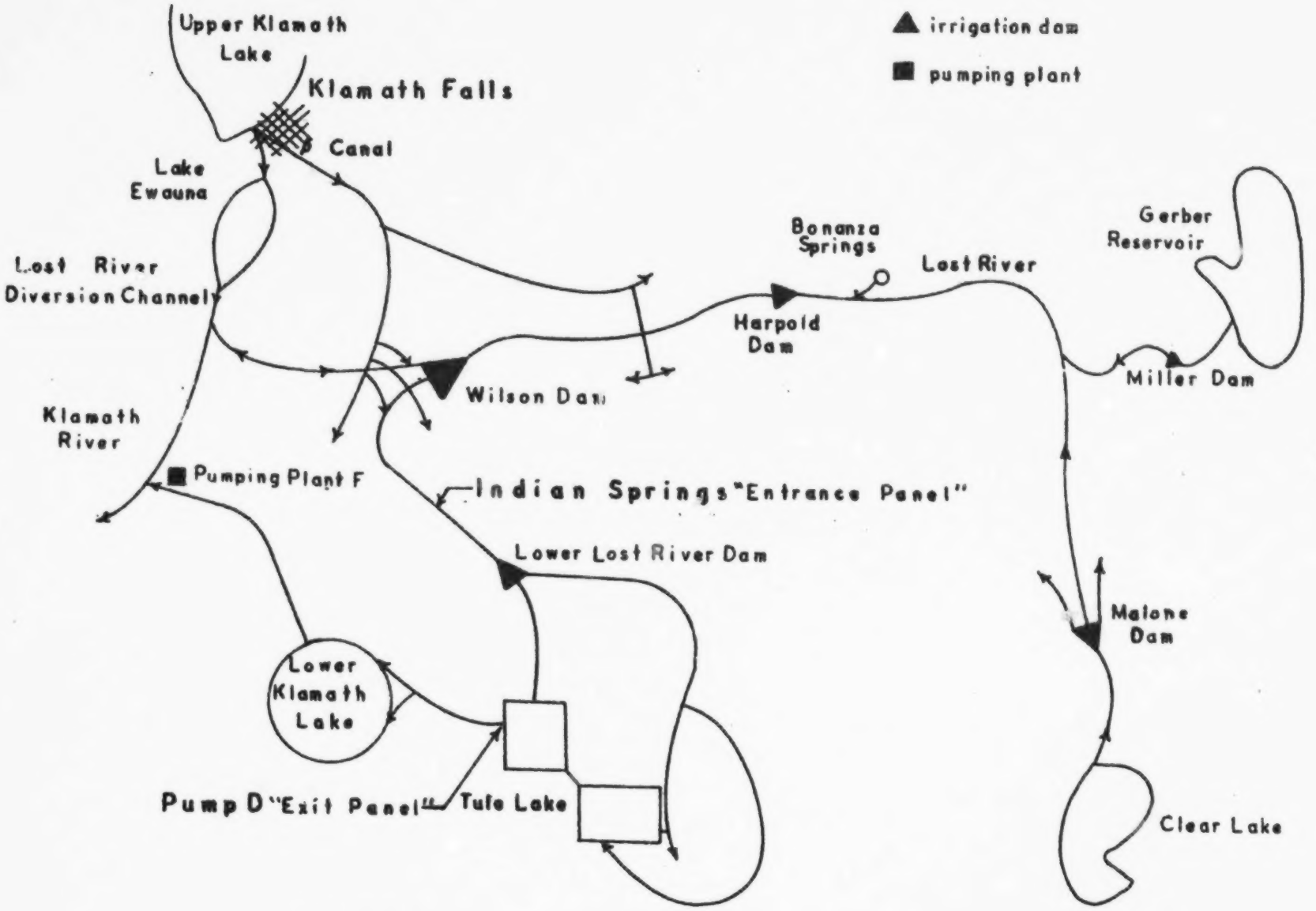

Figure 2 Lost River System

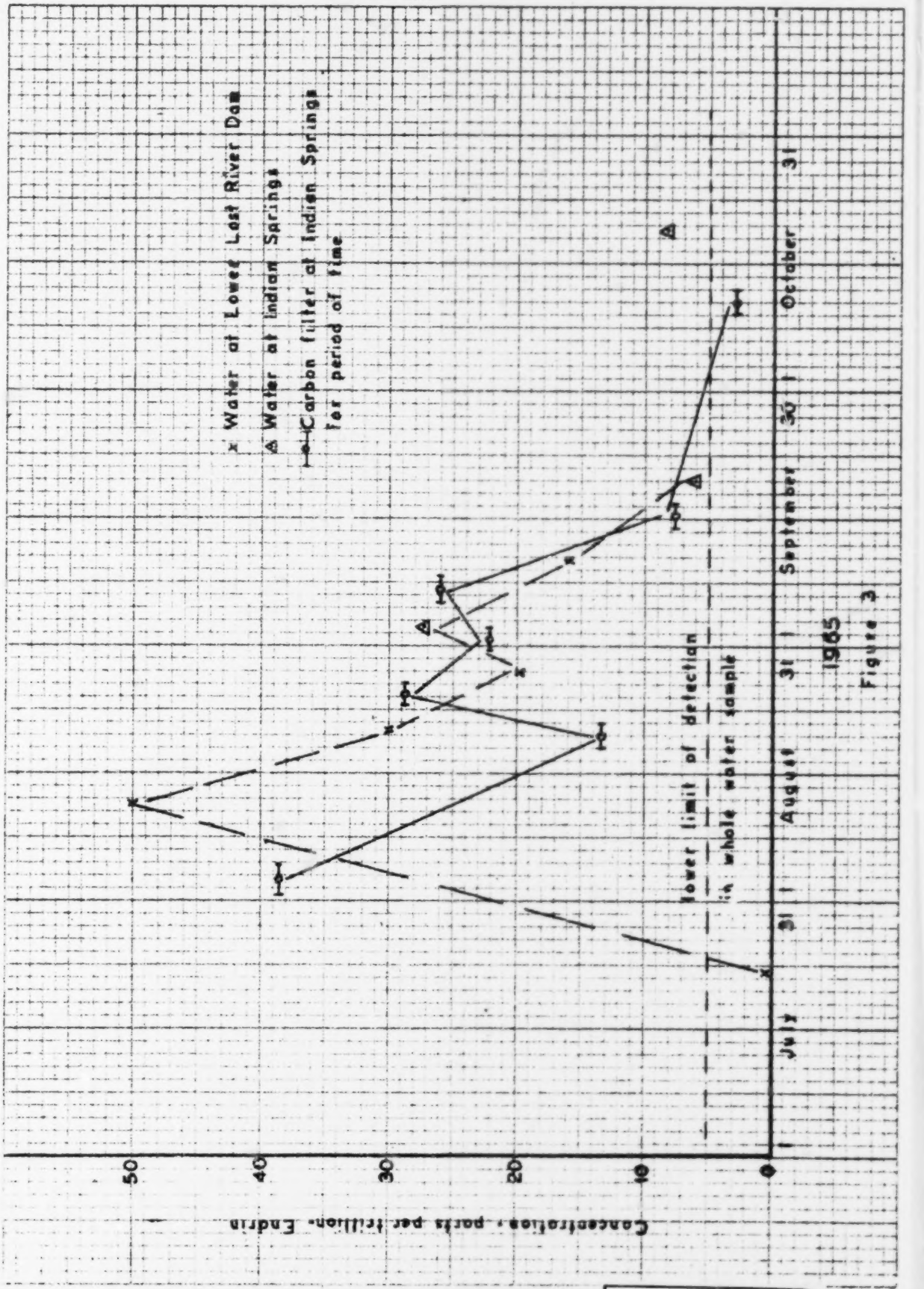

Figure 3

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TABLE I

Summary
Carbon Filters vs Water Samples
Indian Springs - Parts Per Billion

Date	Type of Sample	Size of Sample	Sample Number	Total	DDE	DDD DDT	Heptachlor Epoxide	Dieldrin	Endrin	Aldrin	Other
7/22	Water	4/	237 3/	.133	.01	.01	.007				
7/30-8/4	CAM 1/	1030 L	257		not determined			.002	.037		
8/11	Water		267 3/	.23	.015		.002		.05		
8/16-20	CAM	1248 L	371		.0002	.002	.0004	.0006	.013	.0002	.002
8/20	Water		325 3/	.14	.009		.002		.03		
8/20-26	CAM	1326 L	344		.0005	.003	.001	.001	.029		.001 5/
8/26	Water		330 3/	.033	.007				.020		
8/26-31	CAM	940 L	345		.0014	.0035	.0016	.001	.023		
9/3	Water		369	.14	.007				.020		
9/1-7	CAM	1221 L	372		.0005	.0025 2/	.0005	.001	.024	.0005	.001 5/

1/ Carbon Filter
2/ DDD only
3/ Lower Lost River Diversion Dam
4/ All water samples are 3 liter
5/ Heptachlor
6/ Chlordane

TABLE I (Cont'd)

Date	Type of Sample	Size of Sample	Sample Number	Total	DDE	DDD DDT	Heptachlor Epoxide	Dieldrin	Endrin	Aldrin	Other
9/10	Water		381 3/	.17	.007	.017			.017		
9/22	Water		399	.066	.003	.033	.005		.006		.002 5/
9/22	Water		401 3/	.096	.003	.067	.003		.007		
9/15-22	CAM	2271 L	423		.0002	.0002		.0002	.0074		
10/1	Water		451	.058	.006		.003				
10/1	Water		452 3/	.035							
10/8-13	CAM	956 L	478		.0006	.0027			.0037		.004 6/
10/11	Water		467	.042	.007	.010					.010 6/
10/13-18	CAM	990 L	491		.0005	.0012		.001	.003		.004 6/
10/18	Water		492	.090	.003			.006	.007		
10/18-25	CAM	1377 L	527		.0005	.0007		.0005	.0035		.0067 6/
10/20	Water		512 3/	.047	.019						
10/29-11/5	CAM	1762 L	551		.0002	.0002		.0003	.0003		.0015 6/

1/ Carbon Filter
2/ DDD only
3/ Lower Lost River Diversion Dam
4/ All water samples are 3 liters
5/ Heptachlor
6/ Chlordane

TABLE I (Cont'd)

Date	Type of Sample	Size of Sample	Sample Number	Total	DDE	DDD DDT	Heptachlor Epoxide	Dieldrin	Endrin	Aldrin	Other
11/5-12	CAM	2237 L	561		.0005	.0005		.0005	.0030		.009 6/
11/9	Water		554 3/	.104	.007	.017			.007		.020 6/
11/12-19	CAM	1267 L	566		.00036	.00095					.0001 6/
11/19	Water		567	.090	.003	.017			.007		
11/19-26	CAM	1242 L	582								
12/3	Water		587	.053	.007	.010					
12/3-10	CAM	1312 L	602		.00015	.00016					.0015 6/
12/10	Water		597	.061	.003						.010 6/
1/18	Water		634 3/								

1/ Carbon Filter
2/ DDD only
3/ Lower Lost River Diversion Dam
4/ All water samples are 3 liters
5/ Heptachlor
6/ Chlordane

TABLE II

Summary
Carbon Filter vs Water Samples
Pump D - Parts Per Billion

Date	Type of Sample	Size of Sample	Sample Number	Total	DDE	DDD DDT	Heptachlor Epoxide	Dieldrin	Endrin	Aldrin	Other
4/20	Water 3/		100	.100	.013	.027					.033 2/
4/16-20	CAM 1/	710 L	101			.001					
7/21	Water		228	.09	.010		.001				
7/22-28	CAM 1/	1043 L	247		.001	.001			.0014	.07	.003 4/
10/1	Water		449	.041	.003						
10/1-6	CAM	800 L	462		.0006	.0030			.0025		.0080 2/
10/6-11	CAM	988 L	466		.0005	.0006		.0001	.0020		.0020 2/
10/11	Water		471	.019							
10/11-16	CAM	1782 L	528		.001	.0022		.001	.0022		.013 2/
10/20	Water		516	.062	.007						
10/29-11/4	CAM	816 L	529		.001	.002		.0003	.001		.0075 2/

1/ Carbon Filter
2/ Chlordane like
3/ All water samples are 3 liters
4/ Lindane like

TABLE II (Cont'd)

Date	Type of Sample	Size of Sample	Sample Number	Total	DDE	DDD DDT	Heptachlor Epoxide	Dieldrin	Endrin	Aldrin	Other
11/4-12	CAM	834 L	560		.0011			.0005	.0009		.015 2/
11/9	Water		556	.11	.011	.013					.02 2/
11/12-19	CAM	196 L	586		.0038	.002		.0009	.0009		.027 2/
12/10	Water		600	.025	.003						
12/3-10	CAM	330 L	603		.003	.004					.066 2/

1/ Carbon Filter
2/ Chlordane like
3/ All water samples are 3 liters
4/ Lindane like

TABLE III

RESULTS OF CARBON COLUMN WITH GLASS WOOL

Sample Number	Location	Sample Size	Pesticide	1/	2/	3/
566	Indian Springs	53.6 grams	chlordane like	2	.000085	
			DDE	2		
			DDD and/or DDT	2		
			dieldrin	.23	.00001	
			endrin	1.1	.000047	
		1257 liters	chlordane like	0.0001		50%
			DDE	0.00036		19%
			DDD, DDT	0.00095		8%
			dieldrin	0.0016		1%
			endrin	0.0005		9%
586	Pump "D"	50 grams	chlordane like	4	.001	
			DDE	1	.00025	
			DDD, DDT	.7	.00017	
			dieldrin	none sens 3.6		
			endrin	none sens 7.2		
		196 liters	chlordane like	.027		4%
			DDE	.0038		6%
			DDD, DDT	.002		8%
			dieldrin	.0009		66% 4/
			endrin	.0009		50% 4/

1/ Conventional basis (parts per billion)

2/ Based on all pesticide being water sample (parts per billion)

3/ Pesticide on glass wool as a % of total

4/ Maximum value if level present has been only slightly less than sensitivity